

A STUDY ON INCLUSION FORMATION MECHANISM  
IN ALPHA-LiIO<sub>3</sub> CRYSTALS

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STUDY OF THE INCLUSION FORMATION  
MECHANISM IN  $\alpha$ -LiIO<sub>3</sub> CRYSTALS

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ABSTRACT

This article is concerned with an ultra microscopy study of the spatial distribution of inclusions in  $\alpha$ -LiIO<sub>3</sub> crystals by means of an argon laser beam scanning technique. The effects of crystal dimensions and solution fluid flow on the inclusion formation in the  $\alpha$ -LiIO<sub>3</sub> crystals were observed. It was further shown that the fluid flow plays an important role in the formation of inclusions. The results obtained were further applied and verified by growing a perfect  $\alpha$ -LiIO<sub>3</sub> single crystal. This study may provide an experimental foundation for further theoretical studies on the causes of inclusions.

I. Introduction

Inclusion is a type of defect within a spectacular crystal structure. The existence of the inclusion has severely affected the quality and performance of the crystal. Therefore, the interests pursued by the crystallographers and physicists in their study of the inclusions are no longer limited to a diagnosis [1] of the ore forming conditions, but also the exploration of the inclusion formation mechanisms through both experimental and theoretical approaches. Thus, these approaches may help them control the emerging conditions of this kind of defect in a crystal growth process.

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\* Numbers in margin indicate pagination of foreign text.

In 1956, S. Zerfoss and S. I. Slawson [2] systematically summarized the experimental results of inclusions observed within the crystals. They had observed nine types of natural crystals and 15 types of artificial crystals, in which they had discovered that there was a directional distribution of the inclusions and that the inclusions were formed during the disruption of a growth process. D. Elwell and B. W. Neats [3] proposed in their discussion of the molten process crystal growth mechanism that nonuniformity of growth is the cause of inclusion formation. A. A. Chernov and D. E. Temkin, et al. [4,10,11] made a basic assumption of the existence of a separative pressure within a molten film layer in between a foreign particle and the interface. Furthermore, the color dispersive interactions among the solid phase, liquid phase and gas phase and the Debye interaction were taken into consideration. Thus, the relationship between a critical velocity of forming an inclusion and the crystal growth parameters was theoretically interpreted. With respect to the study of inclusions within the solution grown crystals, only scattered experimental data of inclusions were reported on the KDP and sodium tetraborate crystals. However, a trapping theory of inclusions inside a solution grown crystal has not been reported previously.

In this study, a steady high intensity argon laser beam was used to facilitate an ultra microscopic observation of the inclusions within a large amount of crystals grown under different conditions. Based on the summarized data of the distribution of inclusions, the effects of crystal dimension and fluid flow on the inclusion formation within the  $\alpha$ -LiIO<sub>3</sub> crystals were discussed. It was further shown that the latter effect plays an important role in the inclusion formation mechanism. The results were used to guide a process for growing a large piece of high quality single crystal.

## II. Experimental conditions and methods of observation

### 1. Experimental conditions

An  $\alpha$ - $\text{LiIO}_3$  crystal was grown in aqueous solution by means of a constant temperature evaporation method. The necessary equipment and crystal habits were provided based on the literature [9]. In order to explore a close relationship between an inclusion /80 inside the crystal and its growth conditions and environments (such as temperature, pH value, impurity content and state of fluid flow), a combined experiment was carried out for growing a large crystal. Subsequently, an overall observation of the inclusions inside the crystal was made under a high intensity laser beam. The observations and analyses of the inclusions inside 160 pieces of crystals grown in 27 experiments were carried out. Based on a relationship between the initial summary data of the distribution of inclusions and the growth parameters, a series of comparative experiments on the inclusion formation mechanism were implemented as follows:

1) Comparative temperature experiments--Under the identical pH value, impurity content and state of flow, a solution was subject to a different growth temperature (50-75°C). The effect of temperature on the formation and distribution of inclusions was investigated.

2) Comparative pH experiments--At the temperature of solution (70°C), impurity content and the state of flow were kept constant. The effect of different PH values (3-10) on the inclusion formation and distribution was investigated.

3) Experiments on dimensional effect--The effect of a grain crystal diameter (4.6-46.8mm) was studied under the conditions of identical growth parameters, on the formation and distribution of the inclusions.

4) Experiments of fluid flow effect--The effect of changing state of flow (crystal angular velocity  $\omega = 0, 11, 30$  rpm) on the formation and distribution of the inclusions was studied under the identical conditions of temperature, pH value and purity.

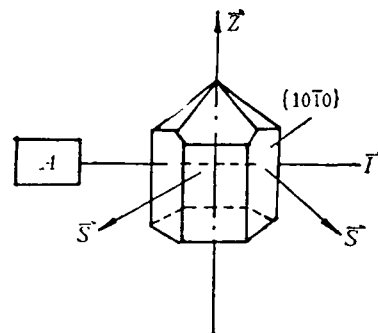
## 2. Methods of observation

M. S. Joshi and B. K. Paul [5] in their study of inclusions inside a KDP crystal, the average density of inclusions was calculated from a deviation between the theoretical mass and the experimental mass of the crystal. The theoretical mass was obtained based upon the structural characteristics of the crystal. Although the accuracy of an experimental result was not too high and only suitable to a special growth condition, however, the result could be used directly for representing the quality of a crystal. In other words, such an experimental method was closely related to the growth of a large crystal.

The ultimate goal of this study was to upgrade the quality of a crystal. Thus, an optical scanning ultra microscopy was chosen based upon the kinetic growth characteristics and growth behavior of the  $\alpha$ -LiIO<sub>3</sub> crystals. The observation and calculation of an average density of the inclusions were achieved through this means. Figure 1 shows the experimental equipment.

Figure 1. Symbols of the experimental equipment

- A--argon ion exciter (laser beam source)
- $\vec{S}$ --direction of observation
- $\vec{Z}$ --optical axis of crystal
- $\vec{I}$ --direction of an incident laser beam



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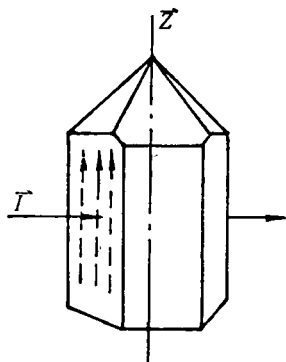


Figure 2. Scanning direction of a laser beam  $\vec{I}$  along  $\{1010\}$  plane

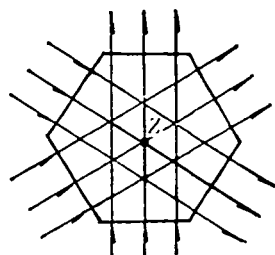


Figure 3. Direction of the 9 scanning beams within the cross sectional plane perpendicular to the Z axis of the crystal

A steady high intensity Ar-laser beam was emitted from a light source A, then through the incident plane  $\{10\bar{1}0\}$ . When the laser beam scanned the crystal along the Z direction, it was possible to observe the distribution of inclusions within the plane parallel to the  $\{11\bar{2}0\}$  plane. Since the experiment was carried out under equal intensity of light beam from the light source, and the observed light spots had an average diameter of  $10^{-2}$  cm, therefore, the number of inclusions can be expressed by an average surface density,  $\bar{n}$ , (number/cm<sup>2</sup>). In order to make the experimental values more representative, the Ar-laser beam was allowed to pass sequentially through three pairs of  $\{10\bar{1}0\}$  crystal planes in the normal direction. Subsequently, each pair of the optical planes was allowed to be scanned from the left zone, middle zone to the right zone along the  $\vec{Z}$  direction as shown in Figure 2. The direction of unmarked arrow dotted lines indicates the scanning direction of the laser beam  $\vec{I}$ . Therefore, the surface density  $\bar{n}$  is the average calculated value from nine planes (as shown in Figure 3). This calculation was achieved after the laser beam had scanned through the nine similar crystal planes parallel to the  $\{11\bar{2}0\}$  plane. This relative number of inclusions more accurately represents the inclusions within a crystal.

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### III. Experimental results

#### 1. Distribution of inclusions

In the experiments, inclusions were observed as a "single inhabitant" and a "group inhabitant" within the  $\alpha$ -LiIO<sub>3</sub> crystals. The dimension, number and distribution of the inclusions are related to the stability and growth parameters of the crystals. The single inhabitant means that the inclusions are scattered randomly in their distribution, while the group inhabitant means that the inclusions are localized and distributed in group fashion. A crystal screen means an oriented group distribution of the inclusions along certain crystal plane. Based on statistical observation of the crystals grown under different conditions, it was found that as a crystal was grown by a static method, probability of distribution of the inclusions was greater in the center section compared to the edge section, while a random unoriented distribution of the inclusions was observed in a crystal grown by the dynamic method. Under the dynamic growth conditions, the group inhabitants inside the crystal did not have a definite location of appearance. Sometimes they appeared in the early stage of transparent crystal right after the formation of a cone; sometimes the inclusions occurred in the latter stage of the growth process. A side view of the crystals showed that at one time the inclusions were located in the middle of the crystals; while at another time they were close to the outside and near the edge of the crystals. In some crystals, there was a crystal screen along the {10 $\bar{1}$ 1} plane. The interfacial stability of these crystals was subject to a greater degree of damage in the course of their growth.

#### 2. Effect of temperature on inclusions

Table 1 shows the results of the comparative growth temperature experiments. In Table 1,  $\omega$  is a rotational velocity of crystal. "+" sign is a positive evidence of inclusion in the crystal



TABLE 1. Results of comparative temperature experiments

experimental number	t (°C)	$\omega$ (rpm)	pH	inclusions
7101	70	0	7	+
7114	75	0	7	+
7118	75	0	7	+
8002	60	0	7	+

TABLE 2. Results of comparative pH experiments

experimental number	pH	t (°C)	$\omega$ (rpm)	inclusions
8006	3	75	0	+
7102	4	75	0	+
7118	7	75	0	+
7119	5	70	0	+
7122	6.5	70	0	+

during the experiments. The experiments showed that under the static state, a crystal grown from neutral solution is not likely to eliminate an inclusion through the change of a growth temperature.

### 3. Effect of pH on inclusions

Table 2 shows the results of comparative solution. pH value experiments under the condition of  $\omega = 0$ . The experiments showed that under a static state it is not likely to eliminate an inclusion through the change of a pH of the solution. S. Matsumura and Y. Uematsa [12] proposed the formation of an inclusion in the  $\alpha$ -LiIO<sub>3</sub> crystal is related to the pH values. However, based on the comparative pH experiments, it is difficult to derive the same conclusion.

TABLE 3. Results of three experiments on the dimensional effect of inclusions

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experimental number	t (°C)	pH	$\omega$ (rpm)	crystal number	$\phi$ (mm)	$\bar{n}$ (number/cm <sup>2</sup> )
8004	65	8	11	3	15.7	0.90
				2	17.4	0.99
				7	33.3	3.38
				4	39.1	8.94
				8	39.9	11.70
8009	70	10	30	8	19.8	1.26
				7	19.9	1.82
				5	21.6	2.45
				3	37.9	2.70
				1	38.5	4.10
8010	75	3	0	3	7.3	0
				4	8.5	0
				5	8.9	0
				13	9.2	0
				7	21.1	5.2
				10	23.3	>10

#### 4. Dimensional effect of inclusions

Table 3 shows the experimental results of the crystal dimensional effects on inclusions. From the table,  $\phi$  is the diametral dimension of a crystal;  $\bar{n}$  is average surface density of the inclusions. Figure 4 is the plotting of  $\bar{n}$  vs.  $\phi$  based on Table 3. It is not difficult to observe that the critical dimension of an  $\alpha$ -LiIO<sub>3</sub> crystal for producing an inclusion is about 10 mm. Also the critical dimension is closely related to the fluid flow effect.

#### 5. Effect of growth rate on inclusions

1) Dimensional effect of growth rate: The experiments showed that under the identical growth conditions, a different dimension of grain crystal has a different rate  $V_z$  of growth. Figure 5 shows the results of two experiments. The experiments indicated that the rate of growth  $V_z$  increases with increasing

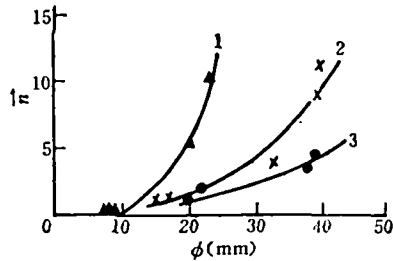
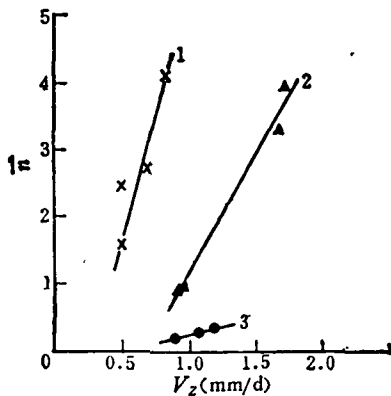


Figure 4. Relationship between the inclusion density and the diametral dimension of a crystal.

1— $\omega=0$ , 2— $\omega=11$ , 3— $\omega=30$



1— $\omega=0$ , 2— $\omega=11$ , 3— $\omega=30$

Figure 6. Relationship curves of growth rate vs. inclusion density.

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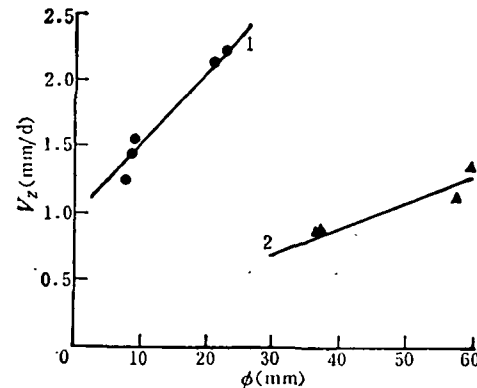


Figure 5. Relationship between the growth rate and dimension of a grain crystal.

1— $\omega=0$ , 2— $\omega=30$

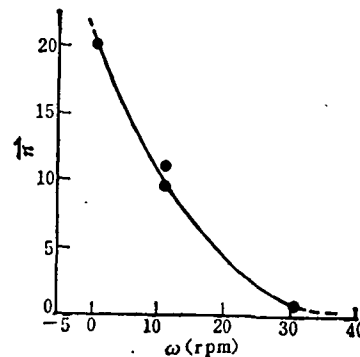


Figure 7. Relationship curves of the inclusion density  $\bar{n}$  vs. crystal rotational velocity  $\omega$ .

crystal dimension. At an angular velocity  $\omega = 30$  rpm, the slope of the curve is less than at  $\omega = 0$ . This reflects the effect of fluid flow on the rate of crystal growth.

## 2) Effect of growth rate on the density of inclusions:

Figure 6 shows a strong effect of the Z--directional growth rate on the inclusions. The crystal growth experiments were shown by three sets of curves having different states of flow ( $\omega = 0$ , 11 and 30 rpm). The curves indicated that the faster the rotation of crystal, the lower the slope of a curve. This again reflects

the effect of fluid flow. By comparing Figures 5 and 6, it was found that the dimensional effect of inclusion formation and the dimensional efficiency of growth rate are closely related.

6. Effect of crystal rotation rate on inclusions: As described previously, the fluid flow experiments on inclusions were carried out under the identical temperature, pH and purity of solution, except the variation in the rates of crystal rotation. However, as the dimensional effect was taken into consideration, the identical crystal dimension must be employed in a comparative study in order to obtain a reliable result.

In the experiments on varying a rotational velocity of crystal ( $\omega = 0, 11, 30$  rpm), other conditions were kept constant such as temperature at  $70^{\circ}\text{C}$ ,  $\text{pH} = 7$  and identical purity of the solution. Besides, the dimension of a grain crystal selected has a diameter  $\phi$ , in the range of  $(39.3 \text{ mm} > \phi > 36.8 \text{ mm})$ . Figure 7 shows the results of experiments. The experiments indicated that the inclusion density decreases with an increase in rotational velocity of a crystal.

#### 4. Analysès and discussions of experiments

The inclusion density  $\bar{n}$  of a crystal is the function of a set of growth parameters ( $t, \text{pH}, \omega, \phi, C$ ) which can be expressed as  $\bar{n} = F(t, \text{pH}, \omega, \phi, C)$ , where  $C$  is the concentration of impurities. Other symbols have been defined previously. Due to the complexity of a crystal growth process and current state of development in this subject, it is still quite difficult to theoretically derive a general function  $F(t, \text{pH}, \omega, \phi, C)$ . However, through the experiment, it is possible to find the major controlling factor of causing the trapped inclusions. Furthermore, the experiments may provide a foundation for establishing a more acceptable functional equation. So far as the  $\alpha\text{-LiIO}_3$  is concerned, what are the major factors? The analysis of the major factors is as follows:

(1) an inclusion within the  $\alpha$ -LiIO<sub>3</sub> crystal is due to the trapping and occlusion of a foreign particle, micro crystal or solution by the interface. The difference between the solution grown process and the molten grown process is that the foreign particles in the solution may cause a solution inclusion. The trapping of an inclusion is related to interfacial instability. Furthermore, the interfacial instability is affected by the growth parameters and their stabilities. From the forementioned comparative temperature experiments, it was shown that at a temperature above 50°C, if the absolute value of a relative temperature fluctuation is less than  $4 \times 10^{-3}$ , then regardless of whether at high growth temperature or low growth temperature, it will not affect the trapping of an inclusion to a significant extent\*.

(2) The literature [9,13] showed that a striking effect of pH values on the growth habit of the  $\alpha$ -LiIO<sub>3</sub> crystals was demonstrated in one experimental phenomenon. Basically, this phenomenon is due to an increase in acid strength resulting in relative suppression of a growth rate in the Z direction. However, from the authors' inclusion related experiments, it was observed that the inclusions were always inside a crystal regardless of the pH values, although at this moment there is no sufficient reason to explain that the interfacial stability is not sensitive to pH values. But it can be predicted that the effect of pH values is not very significant.

Zerfoss and Slawson had attempted to eliminate a crystal screen in NaBrO<sub>3</sub> crystal by varying the pH values. However, their attempt was not successful. This was in agreement with the authors' observations.

(3) The dimensional effect of crystal on the inclusion formation was observed in the experiments first time by the authors.

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\* During the experiments, a temperature fluctuation of the warm bath between 50-75°C had an amplitude  $\Delta t = \pm 0.2^\circ\text{C}$ . Therefore, at 50°C the temperature stability should be  $4 \times 10^{-3}^\circ\text{C}$ . If the bath temperature was higher than 50°C, the stability would be increased accordingly.

Actually, the dimension of a grain crystal  $\phi$  is a geometric parameter but not an independent growth parameter. A large dimension of crystal has a large density of inclusions, which is due to an insufficient supply of solutes on a growth plane. Thus, a "starving" effect can be produced easily resulting in an increase in the induced inclusions. Regarding a quantitative treatment of the dimensional effect which should rely upon an exact solution to a convection-diffusion equation and satisfy the experimental boundary conditions, this article will not deal with this theoretical subject in detail. It is believed that this is the topic of fluid dynamics on the crystal growth.

(4) An impurity was considered as a heterogeneous phase which may be occluded by a crystal or formed as an induced solution inclusion. Undoubtedly, the presence of impurities will increase the density of inclusions. Therefore, in order to improve the quality of crystal, the impurities should be avoided as much as possible. However, the major controlling factor of trapping an inclusion within the crystal is either an impurity effect or a fluid flow effect ? or both of them play an equal weight? Table 4 may help answer this question.

TABLE 4. Comparison of the effects of impurity and fluid flow on the inclusions

experimental number	impurity content % (%)			suspension materials in solution	$\omega$ (rpm)	$\bar{n}$ (number/cm <sup>3</sup> )
	Mg	Na	Ca			
8008	$8 \times 10^{-4}$	0.029	0.018	min.	11	>20
8009	$3 \times 10^{-3}$	0.027	0.018	max.	30	<4

Table 4 shows the comparison of impurity effect and fluid flow effect on the inclusions. The  $M_g$  content in the experiment no. 8009 is 3.8 times greater than the experiment no. 8008. Also the content of suspension materials is maximum in the no. 8009. This seemed to imply that the inclusion density should be higher in the experiment no. 8009. However, the results showed that the experiment no. 8009 has much lower density of inclusions than the

experiment no. 8008. This indicated that the fluid flow is more important than the impurity effect. Based on this fact, it is not difficult to understand why under a static condition the probability of inclusion distribution in the middle part of the crystal is greater than that of the edge section. However, under the state of flow, the distribution of inclusions is in a random manner. A probable reason is that when a rate of crystal rotation reaches certain critical values, the surface stability may be sufficiently high and cause solute to diffuse at the interface. With regard to this problem, further investigation is needed.

## 5. Conclusion

Although the crystal growth parameters such as temperature, degree of super saturation, pH value, impurity content, dimension of a grain crystal and rotational velocity, etc. have an effect on the inclusion density during the formation of  $\alpha$ -LiIO<sub>3</sub> crystals, the fluid flow effect plays the most important role in this aspect. The authors regarded that the exploration of an inclusion formation mechanism of the  $\alpha$ -LiIO<sub>3</sub> crystal should mainly rely upon the fluid flow effect. The optimum condition of fluid dynamics for growing a large  $\alpha$ -LiIO<sub>3</sub> crystal should have an angular velocity  $\omega > 30$  rpm. On the basis of this condition, the authors had succeeded in growing a large, high quality single crystal of  $\alpha$ -LiIO<sub>3</sub>. The single crystal weighed 1212.6 g. with a diameter  $\phi$  of 61.9 mm and the inclusion density  $\bar{n} = 0.28$  number/cm<sup>2</sup>.

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